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## Moulding of sintered hexagonal ferrite material

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<b>(21) International Application Number:</b> PCT/IB95/00926 <b>(22) International Filing Date:</b> 26 October 1995 (26.10.95) <b>(30) Priority Data:</b> 94203319.2 15 November 1994 (15.11.94) EP <b>(34) Countries for which the regional or international application was filed:</b> NL et al. <b>(71) Applicant:</b> PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). <b>(71) Applicant (for SE only):</b> PHILIPS NORDEN AB [SE/SE]; Kottbygatan 5, Kista, S-164 85 Stockholm (SE). <b>(72) Inventors:</b> VAN DER ZAAG, Pieter, Jan; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). VAN DER VALK, Pieter, Johan; Calle Goya, 45, E-19200 Azuqueca de Henares (ES). <b>(74) Agent:</b> VAN DER VEER, Johannis, L.; Internationaal Octroibureau B.V., P.O. Box 220, NL-5600 AE Eindhoven (NL).		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> MOULDING OF SINTERED HEXAGONAL FERRITE MATERIAL		
<b>(57) Abstract</b> <p>The invention relates to a moulding of a sintered hexagonal ferrite material. This moulding is characterized in that the majority of the grains of the material have a monodomain structure. By virtue thereof, the loss factor <math>\tan \delta</math> of this material is much smaller than that of corresponding known materials if said material is used in the frequency range of 100 MHz or higher. The monodomain structure of this material is obtained, in particular, if the average grain size of the material is smaller than 2.8 micrometers. The average grain size preferably ranges between 1.4 micrometers and 2.5 micrometers. Preference is given, in particular, to those ferrite materials whose composition corresponds to the formula <math>Ba_3Me_2Fe_{24}O_{41}</math>, wherein Me stands for one or more divalent ions selected from the group formed by Co, Fe, Mn, Ni, Zn, Mg and <math>(Li.Fe)_{1/2}</math>. Even at very high frequencies, these materials exhibit a small loss factor. The mouldings in accordance with the invention are extremely suitable for use in antennas.</p>		

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## Moulding of sintered hexagonal ferrite material.

The invention relates to a moulding of a sintered hexagonal ferrite material. The invention also relates to a magnetic antenna manufactured from this material.

Mouldings of a sintered hexagonal ferrite material are known per se. They are described, inter alia, in US 2,977,312. This type of materials is generally referred to as "ferroxplana materials", which are described in greater detail in "Philips Technical  
5 Reviews", 18 (1956/1957), pp. 145-154.

The known sintered mouldings have the important disadvantage that the losses are relatively high. Said relatively high losses stand in the way of a general application of these materials. See Adv. Ceram. 16 (1986), pp. 1-4.

10 It is an object of the invention to obviate the above-mentioned disadvantage. The invention more particularly aims at providing a moulding of a sintered hexagonal ferrite material whose losses, particularly the loss factor  $\tan \delta$ , are much smaller than the corresponding losses of the known mouldings. These small losses should occur in particular when the ferrite materials in accordance with the invention are used at very high  
15 frequencies of 100 MHz or more.

These and other objects are achieved by means of a moulding of a hexagonal ferrite material, characterized in that the majority of the grains of the material have a monodomain structure.

In series of experiments which have led to the present invention, it has  
20 been established by Applicants that the magnetic structure of the grains is very important for the loss properties of the relevant ferroxplana materials. For example, experiments have shown that sintered hexagonal ferrite materials comprising grains which have only one magnetic domain exhibit a surprisingly low loss factor  $\tan \delta$ . This applies in particular when these mouldings are used at frequencies of 100 MHz or more. Under these conditions, the  
25 loss factor  $\tan \delta$  can be reduced by a factor of 2 or more. It is noted that the expression "the majority of the grains" is to be understood to mean herein "at least 40% of the grains". It is further noted that grains having a monodomain structure comprise only one magnetic domain.

A preferred embodiment of the moulding in accordance with the invention is characterized in that the average grain size of the material is smaller than 2.8 micrometers.

The average grain size preferably ranges between 1.4 and 2.5 micrometers.

Applicants have observed that at an average grain size of approximately 2.8 micrometers, approximately 90% of the grains have a monodomain structure. A smaller average grain size leads to an increase of this percentage. Percentages of 98% and more are  
5 obtained if the average grain size of the hexagonal ferrite material ranges from 1.4 to 2.5 micrometers. The smallest loss factor is observed in mouldings of sintered hexagonal ferrite material having this average grain size. It has been found that the manufacture of average grain sizes below 1.4 micrometers is relatively laborious and hence expensive. In addition, these small grain sizes do not lead to a further reduction of the loss factor because the  
10 favourable monodomain structure has already been reached. It is noted that the grains of the hexagonal material are plate-shaped. For this reason, the grain size is determined in the plane of the grains. The size of the grains is defined in accordance with the so-called "mean linear intercept" method.

The invention can in principle be applied to all types of hexagonal ferrite  
15 materials such as the so-called W, M and Y ferrites. However, in accordance with a preferred embodiment of the invention, the composition of the material corresponds to the formula  $Ba_3Me_2Fe_{24}O_{41}$ , wherein Me stands for one or more divalent ions selected from the group formed by Co, Fe, Mn, Ni, Zn, Mg and  $(Li.Fe)_{1/2}$ . It has been found that this type of hexagonal ferrite material, also referred to as Z ferrite, can very advantageously be used at  
20 extremely high frequencies of 200 MHz and more. By virtue of the monodomain structure of the grains, this material has a very low loss factor under these conditions.

It is noted that maximally one third of the Ba of the W ferrite can be replaced by Sr, Pb and/or Ca. Z ferrites in which maximally one third of the Ba can be replaced by Sr, Pb and/or Ca also fall within the scope of the present embodiment. It is  
25 further noted that Me is preferably composed of at least 80 at. % Co. The most preferred material is the so-called  $Co_2Z$  ferrite, wherein Me is completely composed of Co. The sintered Z ferrite material in accordance with the invention may further be doped with small quantities of other elements, in particular sintering agents such as  $B_2O_3$ .

The invention also relates to a magnetic antenna. This antenna is  
30 manufactured in accordance with the invention from a sintered hexagonal ferrite material as described hereinabove. Such antennas can very advantageously be used in personal communication systems such as mobile telephones and so-called pagers.

These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

A number of mouldings having the chemical composition  $Ba_3Co_2Fe_{24}O_{41}$  and having different average grain sizes were manufactured as follows. For the starting materials use was made of barium carbonate ( $BaCO_3$ ), cobalt carbonate ( $CoCO_3$ ) and iron oxide ( $Fe_2O_3$ ). To obtain the above-mentioned composition, a mixture of 62.7 g  $BaCO_3$ ,  
5 197.5 g  $Fe_2O_3$  and 25.1 g  $CoCO_3$  were ground in ethyl alcohol for approximately 6 hours. After filtration of the mixed powder, it was dried. Subsequently, the powder thus formed was prefired at 950 °C for 4 hours.

To obtain sintered mouldings having different grain sizes, the fired product thus produced was subdivided into ten fractions, each of which was ground in a  
10 different manner in a liquid. All fractions were first ground with steel balls having a diameter of 13-16 mm for 6 to 12 hours. Five fractions were subsequently subjected to a further grinding operation with steel balls having a diameter of 3 mm for 3-9 hours. After filtering-off and drying, the average grain size of each of the fractions was determined by means of a Fisher measurement.

15 After mixing said fractions with a binder (2% ammonium alginate in demineralised water) the mixture obtained was passed through a sieve and subsequently granulated. Next, each of the granulated fractions was pressed ( $600 \text{ kg/cm}^2$ ) to form square blocks. These blocks were sintered for approximately 1-4 hours at a temperature ranging between 1120 and 1400 °C. Dependent upon the sinter duration, sinter temperature and the  
20 fineness of the grind, the blocks of sintered  $Co_2Z$ -ferrite material had an average grain size ranging between 1.0 and 6.0 micrometers. The combination of shorter sinter times, lower sinter temperatures and longer grinding times results in sintered mouldings having a relatively small grain size.

The average grain size was determined by means of the "mean linear  
25 intercept" method on the basis of scanning electron microscopy (SEM) and microstructure photographs. The average size of the magnetic domains was determined by means of neutron-polarization measurements.

The sintered blocks were subjected to a number of magnetic measurements to determine, inter alia, the loss factor at a frequency of 260 MHz at room  
30 temperature. The results are listed in the Table. The Table shows that the mouldings having an average grain size of 2.8 micrometers or less exhibit a much smaller loss factor than mouldings having a larger average grain size. Mouldings having an average grain size  $d$  (micrometers) in the range from 1.4 to 2.5 micrometers were found to have the smallest loss factor.

Table

	d	tan $\delta$
5	1.36	0.005
	1.78	0.004
	2.31	0.0035
	2.52	0.005
10	2.78	0.01
	3.29	0.021
	4.31	0.025
	5.54	0.022

15 In summary, it is noted that mouldings of sintered hexagonal ferrite material, the majority of the grains of which have a monodomain structure, have a considerably smaller loss factor than corresponding ferrite materials of which at least a substantial part of the grains comprise two or more magnetic domains. By virtue thereof, the hexagonal ferrite materials are extremely suitable for use as an antenna material in personal  
20 communication equipment such as mobile telephones etc.

**CLAIMS:**

1. A moulding of a sintered hexagonal ferrite material, characterized in that the majority of the grains of the material have a monodomain structure.
2. A moulding as claimed in Claim 1, characterized in that the average grain size of the material is smaller than 2.8 micrometers.
- 5 3. A moulding as claimed in Claim 2, characterized in that the average grain size ranges between 1.4 micrometers and 2.5 micrometers.
4. A moulding as claimed in Claim 1, 2 or 3, characterized in that the composition of the material corresponds to the formula  $Ba_3Me_2Fe_{24}O_{41}$ , wherein Me stands for one or more divalent ions selected from the group formed by Co, Fe, Mn, Ni, Zn, Mg  
10 and  $(Li.Fe)_{1/2}$ .
5. A moulding as claimed in Claim 4, characterized in that Me is composed of divalent Co.
6. A magnetic antenna which is manufactured from a sintered hexagonal ferrite material as claimed in any one of the preceding Claims.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 95/00926

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC6: C04B 35/26 // H01F 1/10 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: C04B, H01F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
DIALOG: WPI, CLAIMS		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3895092 A (GIUSEPPE SIRONI ET AL), 15 July 1975 (15.07.75), column 1, line 52 - line 55; column 4, line 39 - line 45 --	1,2
X	FR 2034119 B (UGINE KUHLMANN), 11 December 1970 (11.12.70), page 2, line 25 - line 31 --	1,2
A	US 2977312 A (E.W. GORTER ET AL), 28 March 1961 (28.03.61), claim 1 -- -----	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search <b>11 March 1996</b>		Date of mailing of the international search report <b>14-03-1996</b>
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer <b>May Hallne</b> Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

05/02/96

International application No.

PCT/IB 95/00926

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3895092	15/07/75	AT-B- 323436	10/07/75
		AT-B- 339059	26/09/77
		AT-B- 343080	10/05/78
		AU-B- 468757	22/01/76
		AU-A- 4700372	28/03/74
		BE-A, A- 789187	22/03/73
		CA-A- 990063	01/06/76
		CH-A- 574373	15/04/76
		CH-A- 589570	15/07/77
		DE-A- 2246204	29/03/73
		DE-A- 2359424	06/06/74
		FR-A, B- 2153363	04/05/73
		FR-A, A, B 2208863	28/06/74
		GB-A- 1386505	05/03/75
		GB-A- 1449509	15/09/76
		NL-A- 7212709	27/03/73
NL-A- 7316126	04/06/74		
FR-B- 2034119	11/12/70	BE-A, A- 744215	15/06/70
		DE-A- 2003438	03/09/70
		NL-A- 7000901	11/08/70
US-A- 2977312	28/03/61	DE-B- 1236391	00/00/00
		GB-A- 833053	00/00/00